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## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Curable Filled Cycloaliphatic Epoxy Resin Mixtures

We, CIBA LIMITED, a Swiss Body Corporate, of Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a curable resin mixture, and to electrical insulators manufactured from the resin mixture.

It is known to use fillers in castings from casting resin; in many cases the properties of the casting are significantly changed. Thus, it is possible to improve the mechanical properties and, for example, enhance the Martens heat distortion characteristics, and quite generally to reduce the cost of the casting resin composition. Other not inconsiderable advantages are the diminished shrinkage experienced in curing the casting resin composition and the less pronounced exothermic reaction. However, most of the known fillers have distinct disadvantages. For example, the abrasive effect associated with the inorganic fillers most frequently used by industry and the increase in the specific gravity of the castings are disadvantageous. Above all, the use of resins extended by means of fillers in the electrical industry is limited by their unsatisfactory tracking resistance and arc resistance, as well as by the generally very substantial increase in dissipation. The use of, for example quartz meal, as a filler causes a distinct impairment of the good electrical properties of epoxy casting resins.

To overcome the above-mentioned disadvantages it has already been proposed to use, as fillers for epoxy resins, alumina trihydrate, alkaline earth metal carbonates (German Patent Specification No. 1,189,277) alkaline earth metal sulphates (French Patent Specifi-

cation No. 1,267,518) or alkaline earth metal oxalates (German Patent Specification No. 1,129,694). While the use of these fillers results in castings that have satisfactory tracking resistance and in some cases also satisfactory arc resistance, the dissipation loss angle ( $\delta$ ) is not reduced. On the contrary, this angle is greater than with unfilled casting resin compositions or, for an equal dissipation factor, the arc resistance is insufficient, as is the case with ground chalk. The fillers based on oxalates are, moreover, thermally objectionable because such compounds may decompose at relatively low temperatures. Electrical insulators having a protective coating made from material that has a satisfactory tracking resistance are also known; with such components there is however a considerable risk of the mechanical or chemical bond between coating and base being insufficient, which may cause an increased risk of electric breakdowns. Finally, in German Patent Specification No. 1,137,209, there is disclosed a process for the manufacture of castings by hot-curing casting compositions filled with polyethylene or polypropylene. However, the use of polyethylene or polypropylene results in castings that do not possess satisfactory mechanical properties and arc resistance.

It is also known from Patent Specification No. 629,111 to use as curing agents for epoxy resins (prepared by reacting bisphenol A with epichlorohydrin) triazine derivatives, such as melamine or cyanuric acid or dicyandiamide respectively. In this known use, 10 to at most 35 parts by weight of melamine and/or cyanuric acid or 2 to at most 20 parts by weight of dicyandiamide respectively, per 100 parts by weight of epoxy resin are employed, substantially all of the triazine derivative or of the dicyandiamide reacting with the epoxy

4  
1.5, Specimen 6  
or  
impregnating  
resins

2 acetoguanamine

resin during curing, and none of the unreacted curing agent remaining, as filler, in the cured product.

Furthermore, in German Patent Specification No. 1,115,921 it has been proposed to add to a casting resin mixture containing a triazine epoxy resin, an amine curing agent and an aliphatic diglycidyl ether, as a gas donor having a flame-inhibiting action, up to 50%, based on the weight of the whole resin, of melamine.

It has now been found that the addition, to polyepoxide resins, as filler, of certain nitrogenous compounds, the tracking resistance of the cured resins can surprisingly be lowered very substantially.

Accordingly, the present invention provides a curable resin mixture comprising either a polyepoxide resin containing cycloaliphatic groups but no aromatic groups and a curing agent for the epoxy resins, or a pre-condensate from the resin and a curing agent, and at least 40 parts by weight, preferably of over 50 up to 400 parts by weight, for every 100 parts by weight of the resin, of a nitrogenous compound which is a triazine compound, urea, or a substituted or unsubstituted guanidine or guanidine derivative, or a salt thereof, the nitrogenous compound having a molecular weight not exceeding 1000, having a melting point over 120°C and not being appreciably soluble in the resin component at 120°C.

Compared with polyethylene and polypropylene, the castings made from the resin mixtures of this invention display a distinctly improved arc resistance and better mechanical properties.

It is another advantage of the curable resin mixtures of this invention that even a relatively small addition of the nitrogenous compound to electrically less suitable fillers, such as quartz meal, produces a substantial improvement.

The term "curing" as used in this specification indicates the conversion of the above-mentioned resin systems into insoluble and infusible cross-linked products, in general with simultaneous shaping to furnish shaped products, such as castings, mouldings or laminates, or flat structures, such as lacquer films or cemented products.

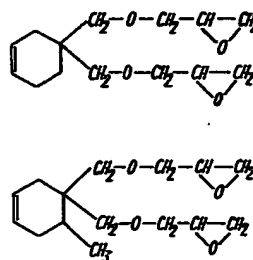
Triazine compounds suitable for use as fillers according to this invention are, for example, ammeline, ammelide, melam, formoguanamine, acetoguanamine, benzoguanamine, monoalkyl - melamines, N - phenylmelamine, mono-, di-, tri-, tetra-, penta- and hexa-

methylmelamines, tetrahydrobenzoguanamine, hexahydrobenzoguanamine and especially cyanuric acid and melamine.

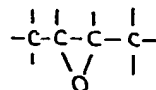
Apart from guanidine itself there may be used as fillers also its salts, for example guanidine carbonate. Good results are obtained especially with substituted guanidines and particularly with dicyandiamide (= 1 - cyano-guanidine).

Suitable resins are compounds with terminal or inner 1,2 - epoxide groups. Particularly suitable terminal 1,2 - epoxide groups are 1,2 - epoxyethyl or 1,2 - epoxypropyl groups. Preferably, there are used 1,2 - epoxypropyl groups linked with an oxygen atom, that is to say glycidyl ether or glycidyl ester groups.

Examples of polyepoxides containing only terminal 1,2 - epoxide groups are those of the formulae:

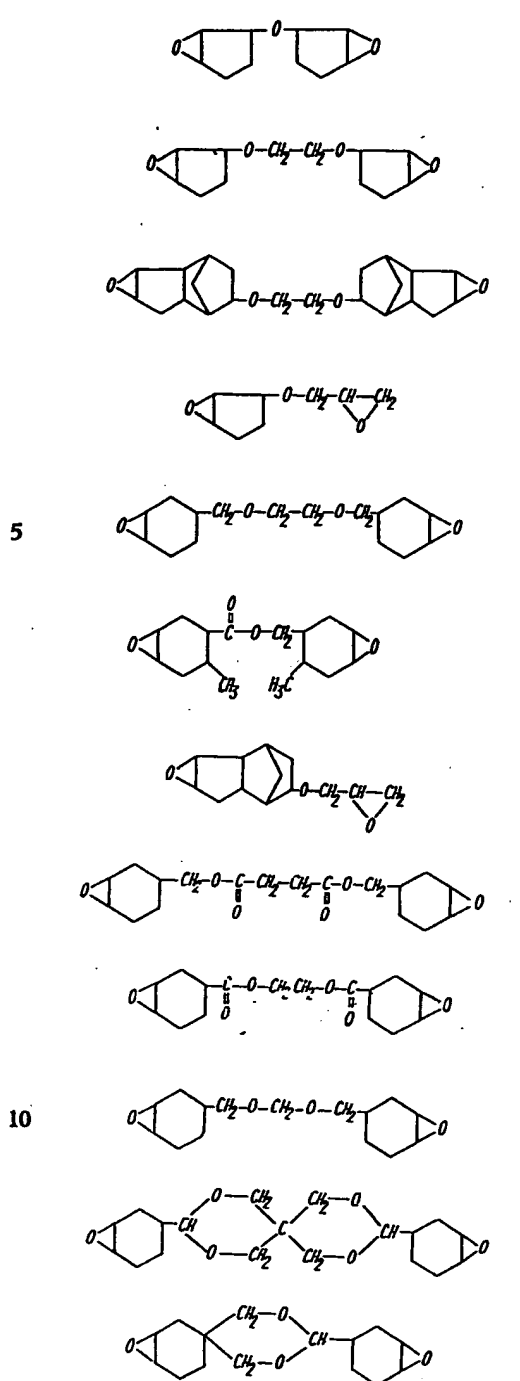


Compounds with inner epoxide groups contain at least one 1,2-epoxide group in an aliphatic chain



or on a cycloaliphatic ring.

Particularly good results are obtained by using resins that contain at least one inner 1,2-epoxide group attached to a cycloaliphatic ring. As examples there may be mentioned epoxidized cyclic dienes such as 1,2,4,5 - diepoxycyclohexane, dicyclopentadiene diepoxide, limonene diepoxide and vinylcyclohexane diepoxide, also cycloaliphatic epoxy ethers, epoxy esters and epoxy acetals containing at least one cycloaliphatic 5- or 6-membered ring to which at least one 1,2-epoxide group is attached, such, for example as the compounds of the following formulae:



15 polymers or telomers, containing epoxide groups, obtained by polymerization or telomerization, respectively, of ethylenically unsaturated monoxepoxides of the cycloaliphatic series, such as 3,4 - epoxycyclohexane - 1,1 - dimethanol acroleinacetal, 3,4 - epoxytetrahydro - dicyclopentadienyl - 8 - allyl ether or 20 3 - vinyl - 2,4 - dioxospiro - (5.5) - 9,10 -

epoxy - undecane, in the presence of a free radical forming polymerization catalyst, such as an organic peroxide, and in this given case, of telogens, such as ketones, can be used.

Mixtures of two or more of the resins listed above can be employed, if desired. 25

For curing the resin, there may be used in principle any known type of curing agent, for example aliphatic, and aromatic primary and secondary and tertiary amines, for instance para - phenylenediamine, bis(para - amino - phenyl)methane, ethylenediamine, N,N - diethylethylenediamine, diethylenetriamine, tetra(hydroxyethyl)diethylenetriamine, triethylenetetramine, N,N - dimethylpropylenediamine; Mannich's bases such as tris(dimethylaminomethyl)phenol; polyamides, for example those from aliphatic polyamines and dimerized or trimerized unsaturated fatty acids; polyhydric phenols, for example resorcinol, (bis(4 - hydroxyphenyl)dimethylmethane, phenol - formaldehyde resins, reaction products of aluminium alcoholates or phenolates with compounds of tautomeric reaction of the acetoacetic acid ester type, Friedel - Crafts catalysts, for example AlCl<sub>3</sub>, SbCl<sub>5</sub>, SnCl<sub>4</sub>, ZnCl<sub>2</sub>, BF<sub>3</sub>, and their complexes with organic compounds, for example BF<sub>3</sub>-amine complexes, metal fluoroborates such as zinc fluoroborate; phosphoric acid; boroxines such as trimethoxyboroxine. 50

Preferred curing agents are polybasic carboxylic acids and their anhydrides, for example phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, endomethylene-tetrahydrophthalic anhydride, methyl - endomethylene - tetrahydrophthalic anhydride (= methyl nadic anhydride), hexachloro - endomethylene - tetrahydrophthalic anhydride, succinic anhydride, adipic anhydride, maleic anhydride, allylsuccinic anhydride, dodecenylsuccinic anhydride; 7 - allylbicyclo(2.2.1)-hept-5-ene-2,3-dicarboxylic anhydride, pyromellitic dianhydride or mixtures of such anhydrides. 55

If desired, there may be additionally used an accelerator, such as a tertiary amine or a salt or quaternary ammonium compound thereof, for example tris(dimethylaminomethyl)phenol, benzyldimethylamine or benzyl dimethyl ammonium phenolate, tin(II)salts of carboxylic acids such as tin(II)octoate or alkali metal alcoholates, for example sodium hexylate. 60

Instead of such polyepoxide resin + curing agent systems there may also be used still soluble and fusible, so-called B-stages obtained by pre-condensing the resin with a suitable curing agent, for example a dicarboxylic anhydride, such as phthalic anhydride. 75

The curable resin mixtures may further contain suitable plasticizers such as dibutylphthalate, dioctylphthalate or tricresylphosphate, inert diluents or so-called active diluents, especially aliphatic or cycloaliphatic mono- 80 85

epoxides, for example butylglycide, cresylglycide, vinylcyclohexene monoxide, 3,4 - epoxy-tetrahydrodicyclopentadienol - 8, 3,4 - epoxy-hexahydrobenzalglycerol or 3,4 - epoxycyclohexane - 1,1 - dimethanol - acroleinacetal.

It is, of course, also possible to incorporate with the curable resin systems to be used according to this invention further conventional additives such as mould lubricants, anti-ageing agents, flame-inhibitors, dyestuffs or pigments.

When a part of the resin is replaced by another epoxy resin, the amount of nitrogenous filler to be added as directed above is calculated from the total weight of the epoxy resin components.

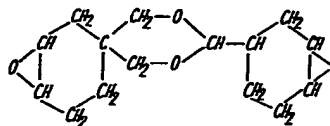
Apart from containing the above nitrogenous compound based on aminoplasts the curable resin mixtures of this invention may contain other known fillers and/or reinforcing agents, for example glass fibres, mica, quartz meal, cellulose, kaolin, ground dolomite, colloidal silica having a large specific surface [AEROSIL ("Aerosil" is a Registered Trade Mark)] or metal powders such as aluminium powder.

The resin mixtures according to this invention are mainly used in the casting resin field. The resulting castings may be used in a wide variety of structural elements, especially in the electrical industry, particularly for instance as high-voltage insulation supports, pin-type and suspension insulators (also on overhead lines), and for insulating components in electrical switchgear such as load shedding switches and quenching chambers, also for grummetts and in the construction of voltage and current transformers. The curable resin mixtures are, however, also very suitable for use in other fields, for instance as laminating resins, bonding agents, moulding compositions, sinter powders, coating compositions, sealing compounds, putties, impregnating and dipping resins.

The invention is illustrated by the following Examples, in which, unless otherwise indicated, parts and percentages in the following Examples are by weight. The relationship between part by volume and part by weight is the same as that between the millilitre and the gram.

#### EXAMPLE 1

12 Parts of a sodium alcoholate solution obtained by dissolving 0.82 part of sodium metal at 120°C in 100 parts of 2,4 - dihydroxy - 3 - hydroxymethylpentane, were dissolved, for tests 1 to 7, in 100 parts of the cycloaliphatic polyepoxy resin (epoxy resin A) of the formula



which contains 6.3 epoxide equivalents per kg. The mixtures were heated to 80°C and 95 parts of the curing agent, hexahydrophthalic anhydride, were fused in. Test specimen 1 contained no filler, whereas specimens 2 to 7 contained the amounts of fillers as shown in the following Table. "Quartzmehl K8" is the trade name of a commercial silica. To determine the properties listed in this Table the specimens were poured at 80°C into aluminium moulds (40 x 10 x 140mm; 130 x 130 x 2mm; 130 x 130 x 4mm), gelled for 4 hours at 80°C and then cured for 12 hours at 120°C.

The more favourable behaviour of the cured specimens 4 to 7 of this invention compared with the cured specimens containing known inorganic fillers (specimens 2 and 3) is readily seen, since the dissipation of the cured specimens of this invention was much lower even at elevated temperatures.

Specimen	1	2	3	4	5	6	7
Epoxy resin A	100	100	100	100	100	100	100
hexahydrophthalic anhydride	95	95	95	95	95	95	95
sodium alcoholate solution	12	12	12	12	12	12	12
Quartzmehl K8		420					
alumina hydrate			350				
melamine				150			
formoguanamine					120		
acetoguanamine						150	
cyanuric acid							140
dissipation factor (tan $\delta$ ) VDE 0303 (50 c.p.s.) in % at 20°C.	0.5	3.8	3.0	0.3	0.2	0.3	0.3
at 100°C.	0.5	6.8	>10	0.3	0.3	0.8	0.3
at 150°C.	0.8	>10	>10	0.8	0.8	2.3	0.3
arc resistance DIN 53484 (stage)	I4	I4	I4	I4	I4	I4	I4
heat distortion point accdg. to Martens DIN 53458, in °C.	182	180	162	154	153	147	170

## EXAMPLE 2

45 Parts of the curing agent phthalic anhydride were fused at 120°C into 100 parts of the epoxy resin A described in Example 1. In addition, in tests 2 to 4 290 parts of "Quartzmehl K8", 290 parts of alumina hydrate, respectively 180 parts of

cyanuric acid, respectively were added as filler. Curing was again performed in aluminium moulds for 4 hours at 120°C and then for 14 hours at 140°C. The test values shown in the following Table clearly prove the superiority of the cured specimen 4, according to this invention.

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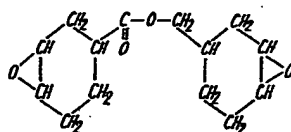
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Specimen	1	2	3	4
Epoxy resin A	100	100	100	100
phthalic anhydride	45	45	45	45
Quartzmehl K8		290		
alumina trihydrate			290	
cyanuric acid				180
Martens heat distortion point (°C.)	152	173	178	206
dissipation factor (tan δ) VDB 0303 (50 c.p.s.) in %				
at 20°C.	1.1	2.8	2.8	0.3
at 100°C.	1.5	5.4	>10	0.4
at 150°C.	1.5	4.7	—	0.5
arc resistance DIN 53484 (stage)	L1	L1	L4	L4

## EXAMPLE 3

52 Parts of phthalic anhydride as curing agent were fused at 120°C into 100 parts each

of the cycloaliphatic polyepoxy resin (epoxy resin B) of the formula



10 containing 7.1 epoxide equivalents per kg, and then the amounts of filler shown in the following Table were admixed. The specimens were poured into aluminium moulds at 120°C as described in Example 1 and cured for 4 hours at 120°C and then for 14 hours at 140°C.

15 Compared with the cured specimens containing known fillers the cured specimens 4 and 5 according to this invention, displayed, in addition to a better Martens heat distortion characteristic, a more satisfactory arc resistance and at the same time much lower dissipation.

Specimen	1	2	3	4	5
Epoxy resin B	100	100	100	100	100
phthalic anhydride	52	52	52	52	52
Quartzmehl K8		350			
alumina trihydrate			350		
melamine				250	
cyanuric acid					125
Martens heat distortion point (°C.)	76	134	152	178	190
dissipation factor (tan δ) VDE 0303, (50 c.p.s.) in % at 20°C.	1.9	4.1	2.2	0.3	0.4
at 100°C.	1.9	6.5	>10	0.5	0.5
at 150°C.	1.6	6.5	—	0.5	0.5
arc resistance DIN 53484 (stage)	L1	L1	L4	L4	L4

## EXAMPLE 4

In tests 1 to 5, 12 parts of the sodium alcoholate solution described in Example 1, 100 parts of epoxy resin B and 105 parts of the curing agent hexahydrophthalic anhydride were melted together at 80°C. In tests 2 to 5, additionally and respectively 400 parts of "Quartzmehl K8", 400 parts of alumina trihydrate and 300 parts of benzoguanamine and 300 parts of melamine were stirred in. The

specimens were poured into aluminium moulds and cured for 4 hours at 80°C and then for 12 hours at 120°C. Compared with the cured specimens 2 and 3, which contained known inorganic fillers, the cured specimens 4 and 5, according to this invention displayed much lower dissipation and have moreover, in contrast to specimen 2, filled with quartz meal, the highest stage 4 of arc resistance.

Specimen	1	2	3	4	5
Epoxy resin B	100	100	100	100	100
hexahydrophthalic anhydride	105	105	105	105	105
sodium alcoholate solution	12	12	12	12	12
Quartzmehl K8		400			
alumina hydrate			400		
benzoguanamine				300	
melamine					300
dissipation factor (tan δ) VDE 0303 (50 c.p.s.) in % at 20°C.	0.4	2.0	3.2	0.4	0.4
at 100°C.	0.4	2.6	13.5	1.5	0.4
arc resistance DIN 53484 (stage)	L4	L1	L4	L4	L4

## EXAMPLE 5

In 100 parts of a polyglycidyl ester resin liquid at room temperature (viscosity 600 centipoises at 25°C; containing 6.3 epoxide equivalents per kg; obtained by reacting epichlorohydrin with hexahydrophthalic acid in the presence of a quaternary ammonium salt, followed by dehydrohalogenation by means of sodium hydroxide solution) there were incorporated, at 120°C, 77 parts of the curing agent phthalic anhydride and then there were added in test 1 300 parts of "Quartzmehl K8" and, in test 2, 150 parts of cyanuric acid. The casting resin mixtures thus obtained were then poured into the aluminium moulds described above and cured for 4 hours at 120°C and then for 24 hours at 140°C.

Both specimens possess good mechanical properties and the specimen 2, according to this invention, displayed in addition a much lower specific gravity and substantially lower dissipation at room temperature ( $\tan \delta$  at 20°C according to VDE 0303: 0.2% compared with 2.0%).

## EXAMPLE 6

When in the process described in Example 5, the hexahydrophthalic acid was replaced by tetrahydrophthalic acid, a polyglycidyl ester resin having a viscosity of 550 centipoises at 25°C and containing 6.42 epoxide equivalents per kg was obtained.

The test specimens were prepared as described in Example 5, with the use of 81 instead of 77 parts of the curing agent phthalic anhydride for every 100 parts of the polyglycidyl ester resin. Again, the specimen of this invention, which contains, as filler, cyanuric acid, displayed at room temperature a considerably improved dissipation factor  $\tan \delta$  (0.2 against 1.3%).

## WHAT WE CLAIM IS:—

1. A curable resin mixture comprising either a polyepoxide resin containing cycloaliphatic groups but no aromatic rings and a curing agent for the epoxy resin, or a precondensate from the resin and a curing agent, and at least 40 parts by weight for every 100 parts by weight of epoxy resin of a nitrogenous compound which is a triazine compound, urea, or a substituted or unsubstituted guanidine or a salt. Thereof, the nitrogenous compound having a molecular weight not exceeding 1000, melting above 120°C and not being appreciably soluble in the resin component at 120°C.
2. A resin mixture according to claim 1, wherein 50 up to 400 parts by weight of the nitrogenous compound is present.

3. A resin mixture according to claim 1 or 2, wherein the nitrogenous compound is melamine.

4. A resin mixture according to claim 1 or 2, wherein the nitrogenous compound is cyanuric acid.

5. A resin mixture according to claim 1 or 2, wherein the nitrogenous compound is dicyandiamide.

6. A resin mixture according to any one of the preceding claims, wherein the resin contains at least one 1,2-epoxide group attached to the cycloaliphatic ring.

7. A resin mixture according to any one of claims 1 to 5 wherein the resin contains at least one glycidyl ether group.

8. A resin mixture according to claim 7 wherein the resin is the diglycidyl ether of tetra- or hexa-hydrophthalic acid.

9. A resin mixture according to any one of the preceding claims wherein a part of the resin is replaced by another epoxy resin.

10. A resin mixture according to claim 1 substantially as described in any one of Examples 1 to 4.

11. A resin mixture according to claim 1 substantially as described in any one of Examples 5 or 6.

12. Electrical insulators manufactured from a resin mixture according to any one of claims 1 to 10.

13. Electrical insulators manufactured from a resin mixture according to claim 11.

14. Insulators according to claim 12, which are electrical overhead lines insulators.

15. Insulators according to claim 13 which are electrical overhead lines insulators.

16. Insulators according to claim 12, which are insulating components of electrical switchgear.

17. Insulators according to claim 13, which are insulating components of electrical switchgear.

18. Insulating components according to claim 16 which are components of load shedding switches or quenching chambers.

19. Insulating components according to claim 17 which are components of load shedding switches or quenching chambers.

20. Insulators according to claim 12 substantially as described herein.

21. Insulators according to claim 13 substantially as described herein.

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